

Reprinted without change of pagination from  
*Journal of Polymer Science, Part B, Polymer Letters*, Vol. 2, No. 1, pp. 117-121, January 1964

pp. 117-121

N64-19959

CODE NINE

NASA CR-53503

*Technical Report No. 32-517*

*Degradation of the  
Polyacenaphthylene-Sodium Complex*

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This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by the National Aeronautics and Space Administration.

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January 1964

DEGRADATION OF THE  
POLYACENAPHTHYLENE-SODIUM COMPLEX\*

It was recently shown (1) that polymers containing several aromatic rings in the side chain may be complexed with alkali metals to yield colored solutions which exhibit a well-resolved electron spin resonance (ESR) signal. The ESR spectrum of the polyacenaphthylene-sodium complex in tetrahydrofuran solution (Fig. 1)<sup>†</sup> has now been found to be identical with the spectrum of acenaphthylene radical anion and, therefore, both spectra are due to the monomeric species. This conclusion is supported by the fact that the visible spectra of the monomer and of the polymer are also very similar (2) and by the discovery that polyacenaphthylene undergoes extensive degradation when reacted with sodium (1). Furthermore, the hyperfine structure of the experimental spectrum (Fig. 1) is consistent with theoretical considerations.

The following four coupling constants ( $A_i$ ) may be found by a trial and error examination of Fig. 1:

$$A_1 = 5.93 \text{ gauss}$$

$$A_2 = 5.00 \text{ gauss}$$

$$A_3 = 3.14 \text{ gauss}$$

$$A_4 = 0.71 \text{ gauss}$$

Setting the central transition field as the arbitrary origin, the "theoretical" spectrum was calculated and shown in Fig. 2. It reproduces the experimental results almost exactly and, therefore, the choice of coupling constants is justified. The connection between theory and experiment is now made using the relationship postulated by McConnell (3):

$$A = Q\rho$$

where  $A$  is the value of the coupling constant,  $Q$  is a semiempirical constant of the order of 20 to 30 gauss for aromatic molecules, and  $\rho$  is the unpaired spin density (on the carbon atom linked to the coupled proton) which may be calculated from molecular orbital theory. The need for a precise value of  $Q$  may be circumvented by comparing the ratios of coupling constants with the ratios of spin densities calculated for acenaphthylene by the approximate HMO theory (4). It may be seen from Table I, where the spin densities are given and their ratios compared with those

\*This paper represents one phase of research performed by the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration, Contract NAS 7-100.

<sup>†</sup>The ESR spectrum was identified by Dr. E. E. Genser and Dr. H. W. Brown.

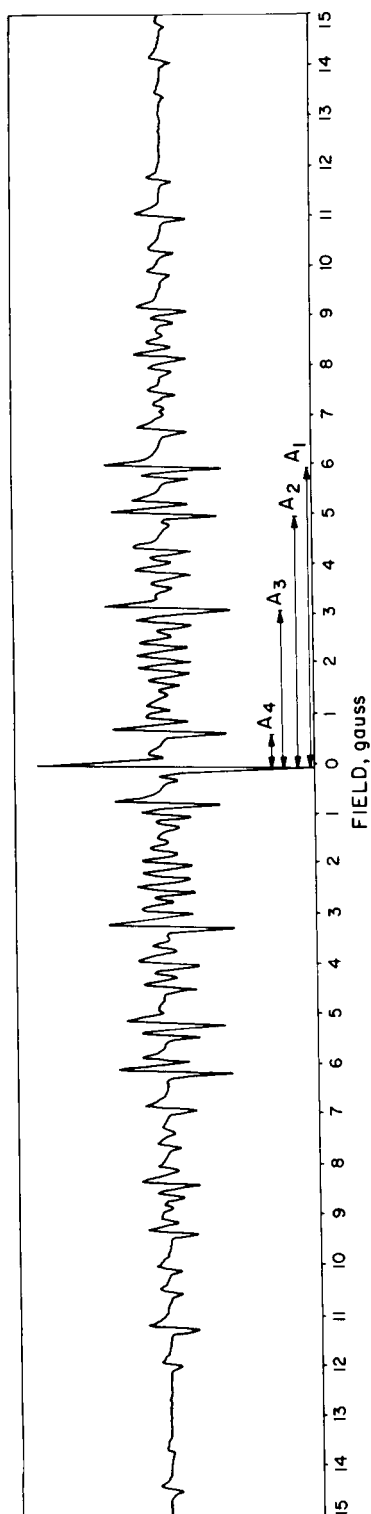


Fig. 1. Experimental ESR spectrum of polyacenaphthylene-sodium complex.

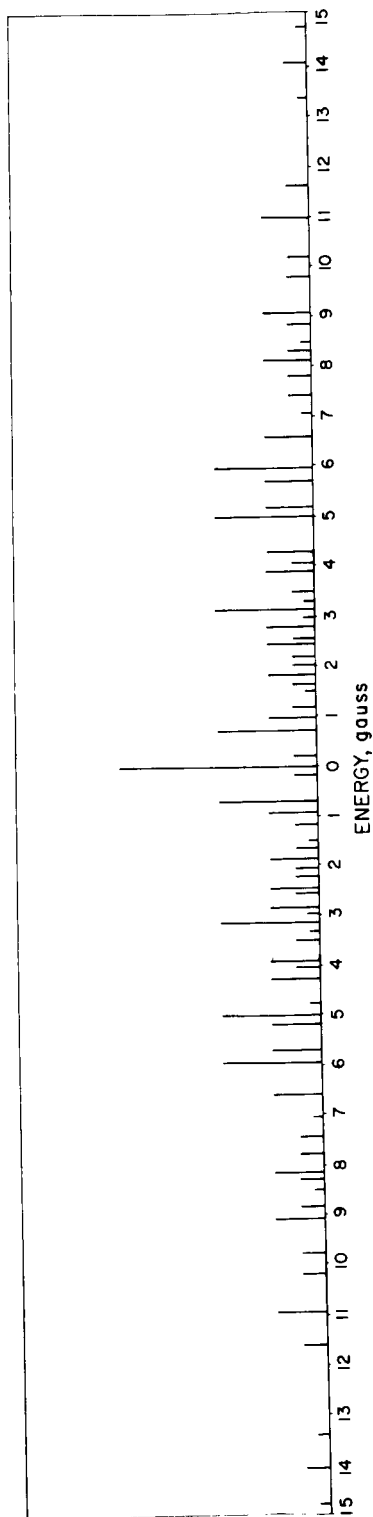


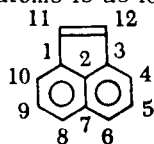
Fig. 2. Calculated ESR spectrum for the acenaphthylene radical anion, intensity in arbitrary units.

TABLE I

Comparison of Calculated Spin Densities with Experimental  
Coupling Constants of Acenaphthylene

Calculated spin densities <sup>a</sup>	Ratios of calculated spin densities	Ratios of experimental coupling constants
$\rho_{11} = \rho_{12} = 0.104$	$\rho_8/\rho_4 = 1.18$	$A_1/A_2 = 1.19$
$\rho_4 = \rho_{10} = 0.151$	$\rho_4/\rho_4 = 1.00$	$A_2/A_2 = 1.00$
$\rho_5 = \rho_9 = 0.014$	$\rho_5/\rho_4 = 0.09$	$A_4/A_2 = 0.14$
$\rho_6 = \rho_8 = 0.178$	$\rho_{11}/\rho_4 = 0.69$	$A_3/A_2 = 0.63$
$\rho_1 = \rho_3 = 0.053$	—	—
$\rho_2 = \rho_7 = 0$	—	—

<sup>a</sup> The numbering of carbon atoms is as follows:

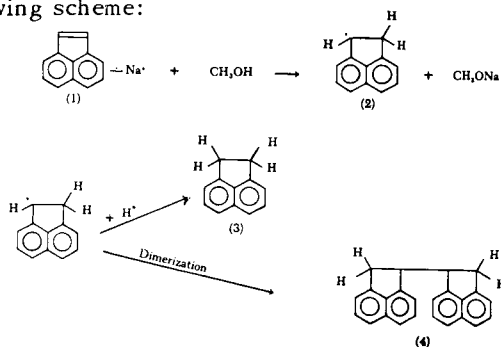


of the experimental coupling constants, that good agreement is obtained between the experimental and theoretical values. Thus the hyperfine coupling constants may be assigned as follows:

$A_1$  ————— protons 6,8  
 $A_2$  ————— protons 4,10  
 $A_3$  ————— protons 11,12  
 $A_4$  ————— protons 5,9

There seems to be little doubt that the electron spin resonance spectrum obtained from polyacenaphthylene-sodium complex is due to the monomeric acenaphthylene radical anion.

Attempts of chemical isolation of acenaphthylene from the degraded polymer were, however, not successful. The acenaphthylene radical anion probably undergoes reduction on addition of methanol in agreement with the following scheme:



According to this mechanism, either acenaphthene (3) or diacenaphthyl (4) is the reaction product. Spectroscopic evidence supports the chemical findings. In Fig. 3 are shown the U.V. spectra of the monomer in methanol (a) and in benzene\* (b), of acenaphthene in methanol (c), and of the methanol extract of the degraded polymer (d). The examination of Fig. 3 rules out the possibility of monomer being the major component in the methanol extract, which however exhibits absorption peaks of the same wavelengths as acenaphthene. As the spectrum of diacenaphthyl is identical with the spectrum of acenaphthene (5), no decision can be made at the present time as to which of the two species is formed. On the basis of the electron spin resonance, the U.V. spectrum, and the chemical results we conclude that polyacenaphthylene in the presence of Na undergoes very rapid bond dissociation with the formation of polymeric anions from which the acenaphthylene radical anion is split off. The latter is reduced to acenaphthene or diacenaphthyl during the process of isolation.

The conclusions concerning the degradation of the polymer are sup-

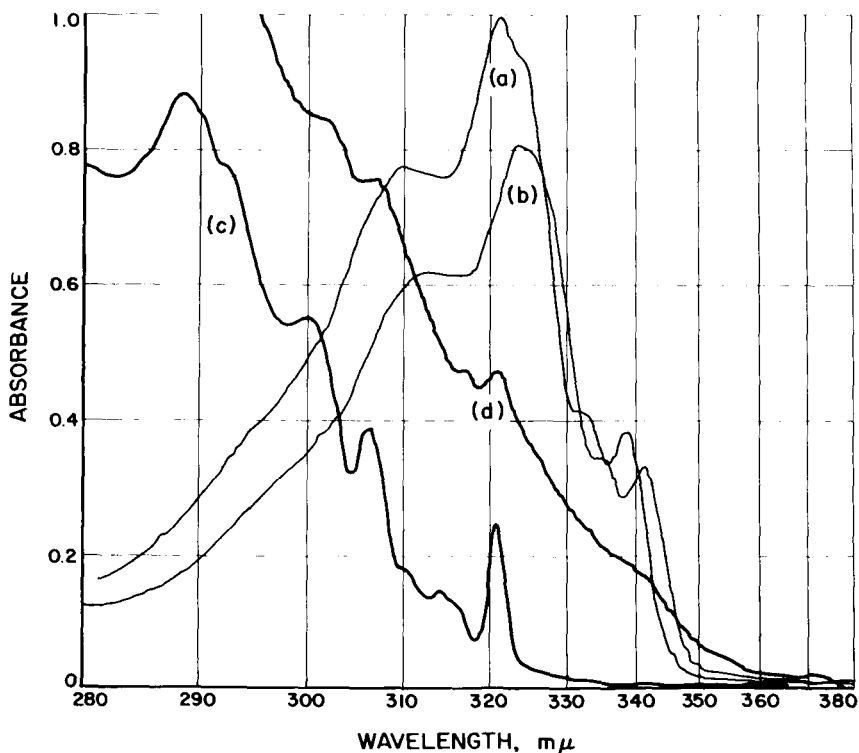


Fig. 3. U.V. spectra of acenaphthylene monomer in methanol (a), in benzene (b), acenaphthene in methanol (c), and methanol extract of the degraded polymer (d).

\*The observed shift in absorption peaks is due to a solvent effect.

ported by the finding that the original weight average molecular weight ( $M_w$ ) of polyacenaphthylene of 500,000 after complexing with sodium (30 mole %) at room temperature for one hour yielded a polymer (99% recovery) of  $M_w = 75,000$ , while the weight of the methanol extract amounted to less than 1%.

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Received September 4, 1963  
Revised October 14, 1963